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CENTRAL INTELLIGENCE AGENCY

REPORT

INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

CD NO.

| | |
|---|---|
| COUNTRY | USSR |
| SUBJECT | Scientific - Photoconductivity |
| HOW PUBLISHED | Monthly periodical |
| WHERE PUBLISHED | Moscow |
| DATE PUBLISHED | Dec 1948 |
| LANGUAGE | Russian |

DATE OF INFORMATION 1948

DATE DIST. 24 Jul 1950

NO. OF PAGES 5

SUPPLEMENT TO REPORT NO.

THIS IS UNEVALUATED INFORMATION

## PHOTOCONDUCTIVITY OF SOME INTERMETALLIC COMPOUNDS

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Submitted 26 Jul 1948

This article discusses the photoconductivity possessed by the intermetallic compounds of fixed composition, $ZnSb$ and $Mg_3Sb_2$; their spectral distribution of photoconductivity is measured. Conclusions are drawn concerning the semiconductive nature of these compounds.

As is well known, the metal anion-producers are located in Groups IV, V, and VI of the periodic system. These elements, when alloyed with metals of the first three groups of the periodic system, give intermetallic phases of constant composition, which phases are characterized by singular points on the composition-property diagram. The composition of such phases is determined by the ordinary rules of valence, but their structure is characteristic of compounds that possess ionic bonds.

A typical representative of this class in the material of antimony-cesium photocathodes.(1)   The formation of an antimony-cesium film consists of (a) the application by vaporization in vacuo, upon the walls of a glass flask, of a thin film of antimony and (b) the treatment of this film with cesium vapors at a temperature of about 200 degrees centigrade. As a result of such treatment, the antimony film changes its properties greatly, is made transparent, acquiring a clear yellow-red color, and sharply increases its resistance (to $10^4$ or $10^5$ times). Both of these phenomena indicate a very strong decrease in the number of free charge-carriers.

A detailed study of the physical properties of such a film leads to the conclusion that the substance of the photocathode is not an alloy of two metals, but is a typical ionic compound with the composition $Cs_3Sb$, corresponding to the stoichiometric formula of normal valence.(2)   This substance ordinarily contains excess atoms of cesium.

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The conduction mechanism of this compound characterizes it as a semiconductor. The temperature dependence of conductivity can be represented by a binomial formula of the type:

$$\sigma = a_1 \cdot \exp(-\Delta E/2kT) + a_2 \cdot \exp(-\Delta E'/2kT).$$

The work of dissociation $\Delta E$ corresponding to the width of the forbidden zone in the energy spectrum of electrons equals approximately 0.8 eV, according to the data of N. D. Morgulis and B. I. Dyatlovitskaya.[3]  The value $\Delta E = 0.67$ eV is given by Luk'yanov and Mazover.[2]  As for the quantity $\Delta E'$, determining the temperature dependence of electroconductivity in the region of low temperature, which (quantity) must apparently be regarded as the work of thermal dissociation of electrons from the admixed atoms in the lattice of $Cs_3Sb$, this quantity equals 0.28 eV.  According to our measurements, the temperature behavior of sigma $\sigma$ for $Cs_3Sb$ is represented in Figure 1; $\Delta E$ and $\Delta E'$ equal 0.7 eV and 0.215 eV, respectively.  The sign of conductivity, determined according to the Hall effect for four samples, is of a "hole" type, which fact agrees with P. G. Borzyak's data.[4]

The semiconductor nature of $Cs_3Sb$ is also confirmed by the presence in it of the internal photoeffect.  Borzyak showed that, at the temperature of liquid air, the conductivity changes by a factor of $10^5$ under intense illumination by nonresolved light from an incandescent lamp.  The spectral distribution of photoconductivity has not been investigated in detail.

Experiments

In the course of our investigations of the electrical properties of intermetallic compounds, photoconductivity was observed in two other compounds of this type; namely, in $Mg_3Sb_2$ and ZnSb.  Taking note of the almost complete absence of data indicating the existence of photoconductivity in intermetallic compounds of fixed composition, except data on $Cs_3Sb$ and $Cs_3Bi$ by P. G. Borzyak [4], we shall try to communicate our results in as brief a form as possible.

The samples of ZnSb were prepared according to a method like that worked out by S. A. Vekshinskiy.[5]  Two point vaporizers are placed under a 12-centimeter long glass plate, with platinum electrodes deposited on it by cathodic vaporization , and vaporize Zn and Sb on the plate, thus forming an alloy of variable composition along the plate. /In view of a grammatical error in the original text, the meaning with regard to the location of platinum electrodes and the fact that they have actually been deposited on the glass plate is somewhat vague./  In the region of the intermetallic compound ZnSb, a sharp fall is observed in electroconductivity of the film corresponding to a factor of $10^7$.  For ordinary alloys of Zn and Sb, one never succeeds in obtaining samples of ZnSb with such values of electrical conductivity.  This is explained by the fact that even insignificant deviations, of the order of 0.01 percent, from the exact stoichiometric composition of ZnSb cause a great concentration of conduction electrons completely masking the salt-like properties of the compound.

Vekshinskiy's method possesses, in this connection, an absolute positive advantage that permits one to carry out very accurate dosages of the components in the alloy and, in principle, to approach as close as desired the composition ZnSb.

Samples of $Mg_3Sb_2$ were prepared by alloying chemically pure preparations of Mg and Sb.  Samples were selected with a composition close to the stoichiometric formula, also samples possessing the least electrical conductivity.  Plate-shaped specimens were cut off from these samples and polished to carry out measurements.  We succeeded in obtaining samples with a specific conductivity of the order of $2.5 \cdot 10^{-5}$ ohm·cm at 20 degrees centigrade.

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Photoconductivity was measured by means of an amplitude-modulated light beam. The light beam was modulated by a thin perforated disk rotating on the axis of a small direct-current motor. The maximum frequency of modulation is 5,000 cycles per second.

The source of the light was a 300-watt incandescent lamp with a straight filament. To record the spectral distribution of photoconductivity, a prismatic monochromator of single-stage resolution with quartz optics was employed.

During illumination of the sample by the modulated light beam, a variable voltage arises in the resistance connected in series with the sample and battery, this voltage under certain conditions being proportional to photoconductivity. This voltage was amplified by a linear amplifier in series with the resistances, with voltage amplification equal approximately to $2 \cdot 10^5$. The amplitude of the variable component at the output of the amplifier was measured by a tube voltmeter of Type VKS-7.

The light beam was focussed on the sample in the form of a thin light probe (sonde) 0.1 to 0.2 millimeters wide. The shifting of this light probe over the surface of the sample of variable composition permitted accurate determination, with respect to the maximum effect, of the position corresponding to the stoichiometric composition. All measurements were conducted at room temperature.

Results of Measurements

Photoconductivity was observed for both ZnSb and $Mg_3Sb_2$. In both cases the photoconductivity was small and only on certain samples did we succeed in investigating photoconductivity in resolved analyzed light for wide apertures of the monochromator. In Figure 2, there is a curve showing the spectral distribution of photoconductivity of ZnSb, reduced to a spectrum of equal intensity. And in Figure 3, there is a similar curve for $Mg_3Sb_2$. On the abscissa axis the wave length is plotted in microns, and on the ordinate axis the photo-current is plotted in arbitrary units. The maximum of photoconductivity of ZnSb is around 0.85 micron; $Mg_3Sb_2$, around 0.8 micron. The red limit of the photoeffect of ZnSb cannot be determined because of the smallness of the effect, but in any case it lies beyond 1.7 micron (0.73 eV); for the red limit of the photoeffect of $Mg_3Sb_2$, a sufficiently valid extrapolation of experimental data gives a value close to 1.5 micron (0.82 eV). The thermal energy of dissociation of the electrons determined from the temperature behavior of electrical conductivity and the Hall effect for ZnSb and $Mg_3Sb_2$ turned out to be 0.6 eV and 0.8 eV, respectively.(6,7) The red limit of the photoeffect gives a somewhat larger value. This corresponds completely to the generalized Frank-Condon principle, from which it follows that the thermal energy of activation is always less than the optical energy of activation.

Figure 4 represents the dependence of the photocurrent upon the electrical field strength in a sample of ZnSb. The photocurrent increases linearly with increasing field strength. Up to E equals 240 volts per centimeter, the photocurrent is strictly proportional, for constant potential to the intensity of illumination, a fact which is also observed for $Mg_3Sb_2$.

The small magnitude of the effect could cause doubt, since the observed phenomenon might be due not to photoconductivity, but to a variation in the sample's temperature under the influence of illumination and thus be a purely thermal effect. However, the absence of any noticeable dependence of the effect upon the frequency of modulation of the light beam, varying within wide limits, and the nonagreement of the spectral distribution of the effect with the spectral distribution of intensity in the spectrum of the lamp serving as the light source indicate that we are dealing with true photoconductivity. It is also necessary to note that photoconductivity in samples of an alloy of variable composition with respect to the Zn and Sb content is observed only in a very narrow region where the composition according to calculation corresponds

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exactly to the stoichiometric formula of the intermetallic compound ZnSb, and the electrical conductivity passes through a minimum. On both sides of this thin region (the extremum), photoconductivity falls sharply and remains unobservable, a fact which is explained by the sharp increase of the original concentration of dark conduction electrons in alloys of other compositions, so that the addition of a small quantity of photolectrons due to internal photoeffect remains imperceptible.

Photoconductivity in ZnSb and $Mg_3Sb_2$ in the visible part of the spectrum indicates the presence of forbidden zones in the energy spectra of these compounds. This must be regarded as an additional indication of their semiconductive nature.

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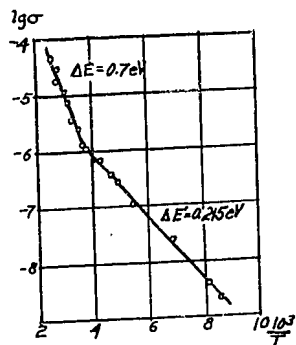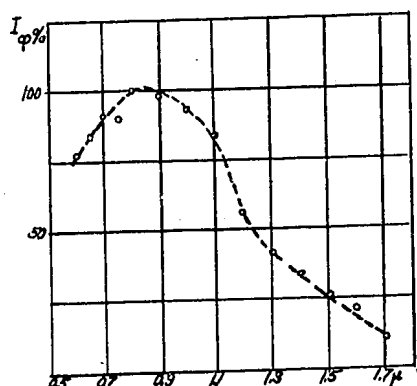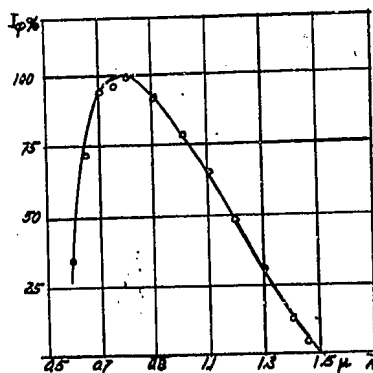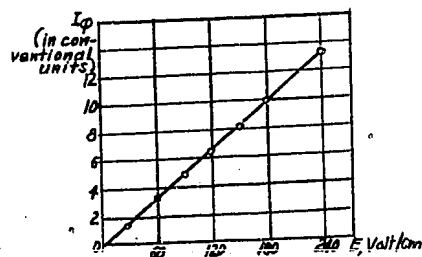/Appended figures follow./

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Figure 1.



Figure 2.  Spectral Distribution
of Photoconductivity
in ZnSb



Figure 3.  Spectral Distribu-
tion of Photocon-
ductivity in
$Mg_3Sb_2$



Figure 4.  Photocurrent
$(I_\varphi)$ versus
Electric Field
Intensity for
the Alloy ZnSb

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